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Piezoresponse force microscopy of ferroelectric thin films: Frequency dependence of phase imaging

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The objective of this work is an evaluation of quantitative measurements of piezoresponse force microscopy for nanoscale characterization of ferroelectric films. To this end, we investigate how the piezoresponse phase difference $\Delta\Phi$ between c domains depends on the frequency ω of the applied ac field much lower than the cantilever first resonance frequency. The main specimen under study was a 102 nm thick film of $\text{Pb}(\text{Zr}_{0.2}\text{Ti}_{0.8})\text{O}_3$. For the sake of comparison, a 100 nm thick PbTiO_3 film was also used. From our measurements, we conclude a frequency dependent behavior $\Delta\Phi \sim \omega^{-1}$, which can only be partially explained by the presence of adsorbates on the surface. © 2008 American Institute of Physics. [DOI: [10.1063/1.2939266](https://doi.org/10.1063/1.2939266)]

I. INTRODUCTION

Ferroelectric thin films are employed in a wide range of applications, among which the most important are nonvolatile memory devices.^{1,2} Ferroelectric materials allow control of the spontaneous polarization direction, which corresponds effectively to a data bit by the application of an external electric field. The corresponding domain wall thickness is typically less than 1 nm.³ Scanning probe techniques offer an attractive possibility to create ultrahigh density data storage (>1 Tbit/in.²),^{4,5} and therefore are an indispensable tool in ferroelectrics research. The electromechanical sensing of ferroelectric nanostructures by atomic force microscopy (AFM) techniques has been successful over the last decade.^{4,5} Up to now reliable studies have been carried out on domain size, domain propagation, in terms of hysteresis loops, and measurement of piezoelectric coefficients.

Piezoresponse force microscopy (PFM) is based on the converse piezoelectric effect, with an AFM probe in contact mode under an applied ac voltage (modulation voltage) generating an alternate electric field, which makes the sample surface vibrate. By a lock-in technique, the amplitude and phase of such electromechanical vibrations are extracted (PRamplitude and PRphase, respectively), providing information on the piezoelectric tensor and magnitude.^{6,7} Nonetheless, the debate on the reliability of the quantitative measurements of PRamplitude and PRphase is still open, and the possible various contributions to the two signals (due to local and nonlocal electrostatic contributions) are still under experimental and theoretical investigation.

Electrostatic contributions strongly affect the piezoresponse signal as has been pointed out in Ref. 6. In addition, clamping effects⁷ and the presence of adsorbates⁸ play a crucial role. Moreover, the presence of a - c domains underneath the tip during local studies has an impact on the measurements of PRamplitude and the value of the piezoelectric coefficient d_{33} .⁹ Indeed, the piezoelectric coefficient d_{33} of

$\text{Pb}(\text{Zr}_{0.2}\text{Ti}_{0.8})\text{O}_3$ (PZT) was found to vary considerably depending on the position of the probing tip on the top electrode for films possessing a $c/a/c$ domain structure, giving values twice the theoretical value for a clamped film by a local movement of ferroelastic $90^\circ a$ domains.⁹

The modulation with frequency of the applied ac voltage of the piezoresponse signal has been proven both for high frequencies (>50 kHz close to the mechanical resonance of the cantilever),⁶ and for low frequencies¹⁰ in the range of 1–50 kHz. However, in the latter case, it stays unclear what the influence is of the driving frequency on the PRphase, and this will be the topic of the present paper. The dependence at low frequencies of the PRphase is considered in combination with various experimental parameters, and possible explanations are outlined.

II. EXPERIMENTAL SETUP AND PROCEDURE

The specimen under study is a commercial 102 nm thick film of $\text{Pb}(\text{Zr}_{0.2}\text{Ti}_{0.8})\text{O}_3$ (001) (Phasis S.a.r.l.) deposited by dc magnetron sputtering on a Nb-doped SrTiO_3 (001) conducting substrate. In addition, another sample is used for comparison purposes, which is a 100 nm thick PbTiO_3 film deposited on a 40 nm thick SrRuO_3 (needed as bottom electrode) and grown on a SrTiO_3 substrate by means of pulsed laser deposition.

Furthermore, the Dimension 3100 (Veeco Instruments) SPM was used for the PFM measurements. The out-of-plane polarization PFM measurements were performed with various cantilevers with different properties, i.e., spring constants, doped or coated tips, in order to evaluate the response under different conditions. The tips have an initial radius of curvature R_{ROC} of approximately 15 nm, which increases up to 50 nm after various PFM measurements due to local damage by operating in contact mode. The applied ac peak-to-peak voltage was varied in the range 1–10 V, with a modulation frequency ranging from 1 to 300 kHz. Contact forces between 0.8 and 5 μN were applied, which are sufficiently weak to avoid any significant local depolarization. PRphase frequency dependence measurements have been performed

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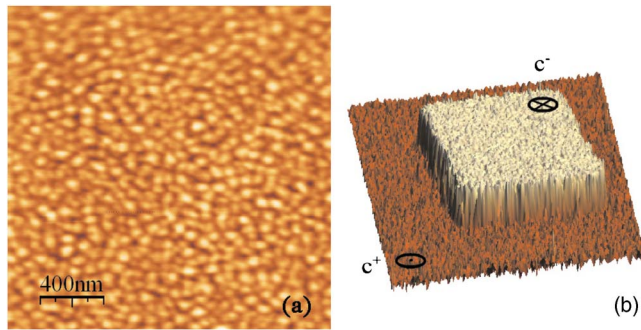


FIG. 1. (Color online) (a) Topography and (b) PRphase image of the investigated area.

in scanning mode, detecting and imaging only the PRphase over an area with both up and down polarized ferroelectric domains as shown in Fig. 1.

III. RESULTS AND DISCUSSION

All the results shown in this section, if it is not otherwise specified, are obtained by measurements performed on the PZT sample. Figure 2 shows the PRphase difference between up-down domains, depicting the influence of two cantilevers with different spring constants. As shown in Ref. 6, the PRamplitude is the sum of the electromechanical contribution (pure piezoelectric effect) and local and nonlocal electrostatic contributions, resulting in a PRphase difference smaller than 180° , which otherwise would be obtained for a pure electromechanical signal. Nonlocal contributions arising from buckling of the cantilever due to capacitor formation between cantilever and tip are inversely proportional to the cantilever spring constant.⁶ This implies a lower electrostatic effect using stiffer cantilevers, resulting also in a higher PRphase. This is confirmed for a $k \sim 42$ N/m [tapping mode etched silicon probe (TESP) tip composed of Sb-doped Si, which is usually used in amplitude modulation or tapping mode AFM] in comparison to a $k \sim 3$ N/m cantilever [force

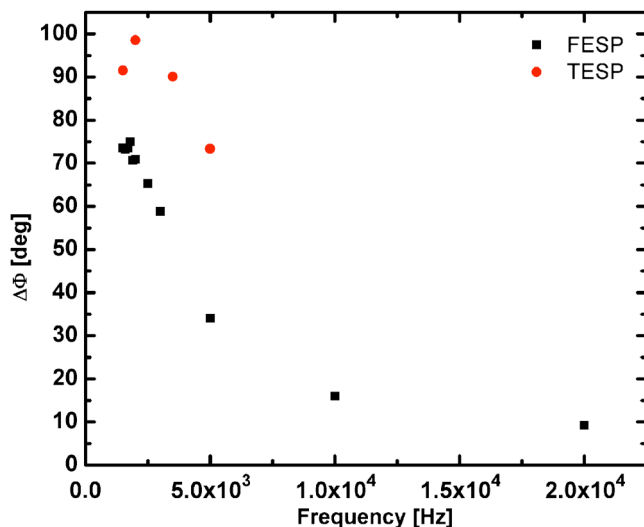


FIG. 2. (Color online) Plot of PRphase difference vs frequency of the modulation voltage (amplitude 3 V), showing values obtained with FESP ($k \sim 3$ N/m and $F_{\text{con}} \sim 700$ nN) and TESP ($k \sim 42$ N/m and $F_{\text{con}} \sim 800$ nN) tips. The PRphase $\Delta\Phi$ using a stiffer tip is remarkably higher.

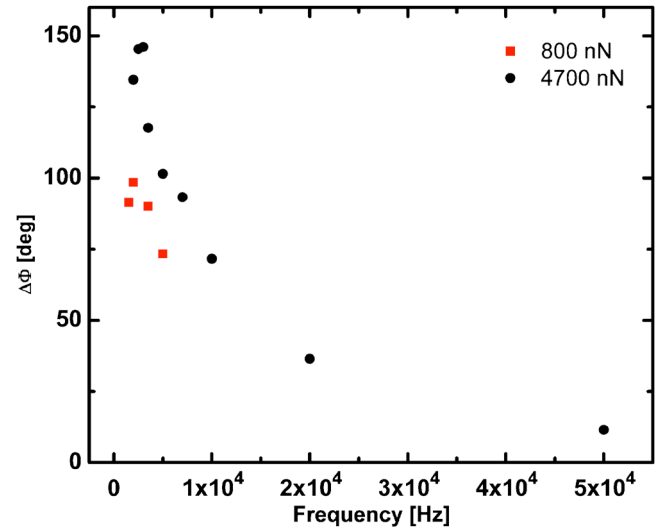


FIG. 3. (Color online) PRphase difference vs frequency of the modulation voltage, applying different contact forces. For a higher force, $\Delta\Phi$ is also increased. Here we used TESP tips and an amplitude of modulation voltage of 3 V.

modulation etched silicon probe (FESP) tip; same material]. For both cases, the PRphase decreases with increasing frequency ω of the driving ac voltage and at a faster rate for the softer cantilevers.

In Fig. 3, we compare the PRphase data obtained by applying different contact forces (F_{con}). It is evident that higher forces ensure a better contact and therefore a higher electromechanical contribution. In general, the voltage applied to the ferroelectric film by the tip, V_{tip} , can be smaller than the voltage difference between the tip and the bottom electrode due to the presence of an adsorbate layer on the film surface, preventing it from a direct contact with the tip. The existence of this dielectric gap with the thickness $w \approx 0.1$ –1 nm and permittivity $\epsilon_w \approx 10$ –100 leads to a significant potential drop between the tip and the surface of a high permittivity ferroelectric layer given by $\tilde{V} \approx V_{\text{tip}}/[1 + (w\epsilon/\epsilon_w R_{\text{ROC}})]$.^{5,6} For our experimental conditions with $R_{\text{ROC}} = 15$ nm, ϵ (for PZT) ~ 1200 , and $w = 1$ nm, i.e., a relatively thick layer of adsorbates, we obtain $\tilde{V} \approx (0.1$ – $0.6) V_{\text{tip}}$ (if $\epsilon_w \approx 10$ –100). Therefore, a significant force F_{con} on the AFM tip is required to penetrate through the adsorbate layer.

However, the force F_{con} has to be lower than the critical value for which the film starts plastically to deform. In other words, we must have $E > F_{\text{con}}/\pi R_{\text{ROC}}^2$, with E the Young's modulus of the ferroelectric film. An approximate calculation for $F_{\text{con}} = 2$ μ N and $R_{\text{ROC}} = 15$ nm, which are typical experimental conditions, yields an exerted pressure of ~ 2.8 GPa. This value is well below $E = 63$ GPa for bulk PZT,¹¹ and therefore, any plastic deformation can be avoided. Note that the mechanical properties of PZT thin films can be different from those of bulk PZT. In the past, studies have shown that the elastic modulus of PZT films ranged from 90 to 160 GPa and the hardness ranged from 9 to 18 GPa, whereas the hardness of bulk PZT was between 7 and 8 GPa.¹¹ Moreover, these studies^{11(c)} indicated that a severe plastic deformation is likely to occur when the calculated contact pressure is higher than the film hardness, which is not the case in our

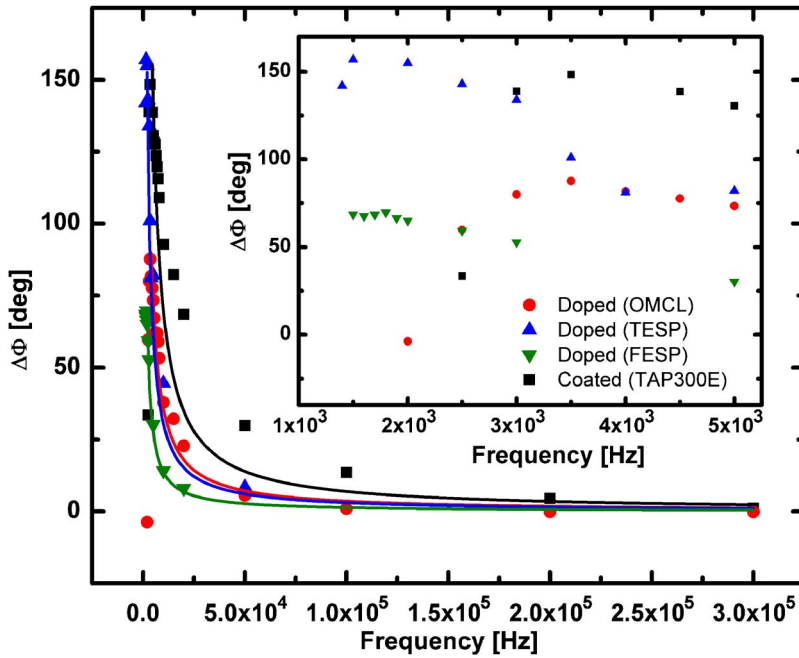


FIG. 4. (Color online) PRphase difference vs frequency of the modulation voltage; data obtained by using different tips. Conditions: 4 V voltage amplitude and $F_{\text{con}} \sim 900$ nN for OMCL (uncoated Si) and TAP300E (gold coated) tip; 7.5 V amplitude and $F_{\text{con}} \sim 3700$ nN for TESP tip (uncoated); 3 V amplitude and $F_{\text{con}} \sim 700$ nN for FESP tip. The fitting (lines in the figure) by means of $\Delta\Phi = a/\omega$ gives values of the parameter a confirming that coated tips give a higher response: 10^5 (TAP300E), 3.8×10^4 (TESP), 3.9×10^4 (OMCL), and 1.6×10^4 (FESP). The inset shows a magnification of the peak area. The higher the contact force and the spring constant, the higher the peak value.

study. In any case, with the applied forces in this study, the tip penetrates fully through the adsorbate layer, measuring therefore a response in which the electromechanical contribution is supposed to be the dominant one.

The frequency dependence of the PRphase for tips coated with different materials (*n*-type Si and Au coated Si) is depicted in Fig. 4. The phase difference obtained with coated cantilevers is significantly higher, which is attributed to the different work functions between the materials, resulting in different electrostatic contributions. A maximum of the PRphase occurs for frequencies about 3 kHz as can be clearly seen in the inset of Fig. 4. After the maximum occurs, the PRphase difference decreases for increasing modulation frequency. As a comparison, Fig. 5 shows the frequency de-

pendence measurement performed on the PbTiO₃ (PTO) sample, which reveals the same trend as that for the PZT sample. This observation proves that such a trend is typical for PFM measurements. Moreover, the characteristic behavior of the PRphase difference versus frequency is fitted by a model that will be analyzed in the following.

The drop in PRphase difference can be partially explained by the presence of adsorbates on the surface of the ferroelectric film.¹² It is tempting to describe the film plus the adsorbates by a series *RC* electric circuit with two capacitors in series. Under the influence of an alternate voltage, this circuit induces a phase shift in the charge response over the circuit itself. Since the adsorbates have different chemical and physical characteristics depending on their charge and nature, the adsorbates over a c^+ (polarization vector upwards) and a c^- (polarization vector downwards) domain are represented by different capacitors, leading to a different phase shift over different domains. The phase shift for each domain is given by $\Phi_i = \arctan[1/\omega RC_i]$, where $1/C_i = (1/C_{\text{ai}}) + (1/C_f)$, with C_f the film capacitance, C_{ai} the adsorbate capacitance, R the resistance of tip-surface junction, and ω the frequency of the ac voltage. i is the index for the adsorbates of c^+ and c^- domains. Although fitting of the PRphase versus frequency is possible with $\Delta\Phi = \Phi_+ - \Phi_-$, it is cumbersome to attain precise information due to the various unknown parameters. Nonetheless, this model indicates that the PRphase decreases with increasing frequency. Additional contributions could arise by the charging/discharging of surface states,^{10,13} which can complicate further the analysis of the PRphase data.

To avoid fitting ambiguities, we considered a simpler analysis in describing the PRphase data in terms of a simple power law of the form $\Delta\Phi = a/\omega^c$. If $\omega RC > 1$, we obtain upon series expansion $\Delta\Phi = \arctan[1/\omega RC] \approx 1/\omega RC - 1/3(\omega RC)^3 + \dots$, where the lowest order term suggests a plausible form for the PRphase $\Delta\Phi$. Also, in Ref. 6, an in-

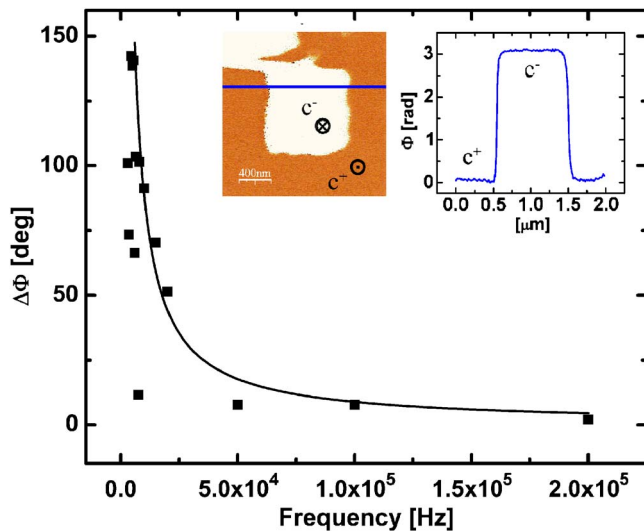


FIG. 5. (Color online) PRphase difference vs frequency of the modulation voltage; data obtained on the PTO sample. Conditions: 4 V voltage amplitude and $F_{\text{con}} \sim 850$ nN using a TESP tip. The fitting gives a parameter a of 10^5 . The inset shows the PRphase image of a $2 \times 2 \mu\text{m}^2$ written area and relative PRphase profile.

verse frequency dependence of the PRamplitude was predicted due to the influence of the cantilever's stiffness with increasing frequency. Furthermore, as the fits in Fig. 4 indicate, the PRphase decrement with frequency follows an inverse frequency dependence with $c=1$. Except for the Au coated tip in Fig. 4, for the other three tips, the value of $a \approx 10^4$ is obtained, indicating similar RC circuit characteristics if we assign $a \approx 1/RC$. The latter yields $RC \approx 10^{-4} - 10^{-5}$ s for all tips considered here. Since the time constant RC determines how fast the system capacitor charges/discharges, this time is related to the polarization reversal of the ferroelectric. Indeed, for a variety of ferroelectric films, a polarization switching time up to tens of microseconds has been observed, while faster switching times are also possible.¹⁴ Therefore, the RC values calculated via the fit are reasonable if compared with results from literature.¹⁴ Note that we had no switching during the measurements since the modulation ac voltage was kept low enough.

Nevertheless, this form for $\Delta\Phi$ alone cannot account for the observed maximum at lower frequencies, indicating that the previous analysis based on a simple inverse power law $\sim 1/\omega$ is limited in the range of frequencies above the observed maximum. In fact, the fits from Fig. 4 give the same parameter a for measurements with the TESP, FESP, and OMCL (Olympus micro cantilever tip composed of n -type single crystal silicon lightly doped with phosphorus, usually used in tapping mode AFM) tips, while the inset shows that the frequency at which the maximum in PRphase difference occurs can be different (1.5 kHz for FESP and TESP, and 3.5 kHz for OMCL). What can be inferred is that the maximum increases with increasing contact force and cantilever stiffness employed for the experiment as is already shown in Figs. 2 and 3. The former enables the measurement to be performed closer to the film surface, increasing the actual electric field on the investigated area and bypassing the adsorbate layer, while the latter reduces the effect of nonlocal electrostatic interaction, leading to data in which the electromechanical interaction is more dominant. As a result, the obtained $\Delta\Phi$ is closer to the theoretical value of 180° , in agreement with other former studies.⁶

Our data show clearly that the PRphase decreases with increasing frequency as a result of field variations due to the presence of adsorbates, which reduces the actual field across the ferroelectric film. Therefore any quantitative determination of field-related material parameter (as required for the verification of semiempirical models of the ferroelectric limit) typically relies on an overestimated field across the sample, while adsorbates reduce this field in a manner that almost decays inversely with frequency dependent fields.

IV. CONCLUSIONS

PRphase difference frequency dependence is analyzed under different experimental conditions. In all cases, an inverse dependence of PRphase difference versus frequency has been observed, with a maximum at low frequencies. A simple fitting of the form $\Delta\Phi = a/\omega$ gives information about the rate of decrement for frequencies above the peak posi-

tion. The analysis of the peak height aids in understanding the influence of the various experimental parameters on the PRphase difference. The electrostatic interaction and electric field weakening (tested by varying cantilever spring constant and contact force) are responsible for a reduction in these values. These two effects indicate the presence of adsorbates on the material surface, which is also proven by independent surface potential imaging. The latter shows for $c+/c-$ domains the inverse potential as expected for polarization charges alone. Nonetheless, the differences in the work function between tip and material, the clamping effect of the surrounding areas not excited by the modulation field, and the mechanical background give additional contributions to the measurements. Hence the necessity emerges of understanding and removing the influence of adsorbates (i.e., by experiments in vacuum combined with *in situ* heating treatments⁸) in order to be able to evaluate the influence of other contributions arising from charging and discharging of surface states.

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